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Studies by Near Edge X-ray Absorption Spectroscopies of Bonding Dynamics at the Graphene/Guanine Interface – A Proposal for High Mobility, Organic Graphene Field Effect Transistors

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14. ABSTRACT

This project was a study of DNA-based polymers (specifically guanine) as gate dielectrics in organic FETs, to examine the molecular arrangement of guanine on graphene via synchrotron spectroscopy. 1 and 4 ML graphene samples stamped on Silicon Carbide (SiC) were examined using two possible substrate terminations. The result showed that CVD-grown graphene transferred to SiC substrates seems electronically healthy; the choice of substrate termination makes little difference to the 4ML graphene but 1ML graphene most closely resembles native graphene on SiC when used with the Si-terminated surface. Structural and chemical analysis suggest healthy dielectric epilayers, suggesting further exploration.

15. SUBJECT TERMS

EOARD, graphene, guanine, GFET

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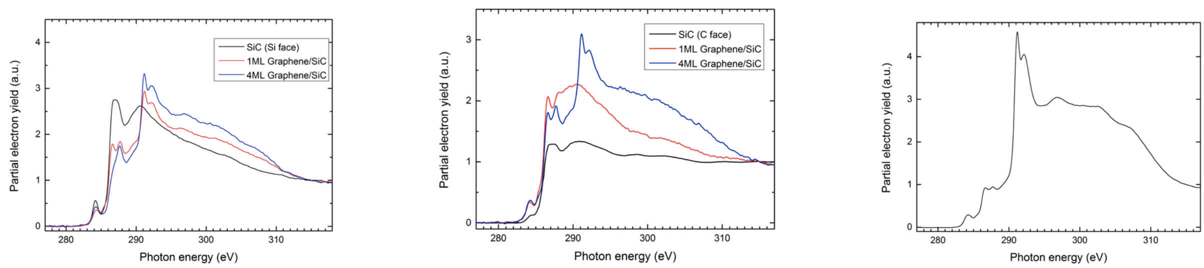
Abstract/ Background

NEXAFS spectra reported here were acquired at the C-k edge at NSLS-I, beam line U8b. The spectroscopic study lead by the Laboratory for Matter Dynamics (Bangor University and University of Texas at San Antonio) is the initial result of a collaborative between NIST (beam line managers), Synchrotron Reserch (detector developers), and Wright Patterson-Air Force Research Laboratories (whom provided the samples). This project has been funded in part by **AFOSR Grant FA9550-14-1-0099,** the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No**. DE-AC02-98CH10886,** and an incipient computational effort around graphene nanointerfaces is funded by a High Power Computing Wales/Fujitsu Fellowship secured by the LMD, which features an on-going collaborative with the Molecular Foundry at Lawrence Berkeley National Laboratories.

Figure 1 below features a comparative analysis of 1 and 4 ML graphene stamped on SiC; where the two possible substrate terminations are considered: Si face (left), carbon face (center), as well as natively grown graphene on SiC (right).

The π* emissions from C=C at 285 eV is clearly resolved, suggesting good quality graphene in all systems in Figure 1. Presence of π* C=C emissions on pristine substrates could point towards a chemically defective substrate preparation prior to graphene deposition. However, the question remains as to the similarity between the analyzed substrates and the substrates used inmediately prior to deposition.

Emissions at ~287 and 288 eV are typically assinged to σ* C-H and π* C=O respectively. Decreased intensities at 287 eV at 4ML for Si termination (Figure 1 left) suggests that C-H impurities could in fact be in the substrate. Conversely, π* C=O signal ~ 288eV has a diminished intensity in the substrate and increases with graphene in both terminations (Figure 1 left and center), suggesting an impurity adsorbed to the graphitic structure.
Emissions σ* C-C and C-Si from substrate will lie at similar energies within the 291-294 eV, and to the former, both SiC and graphene will contribute; albeit with different spectral fingerprints as seen in Figure 1. In fact, the σ*C-Si from the substrate can be seen in all graphene spectra in Figure 1 as an additional shoulder around 290 eV,prior to the typical σ*C-C double peak of graphene at around 292-294 eV.



Epitaxially-grown graphene on SiC (Figure 1 left) shows the typical rich structure at energies > 292 eV, suggesting optimum growth, inclusive of the expected σ* C-H and π* C=O emissions, with lower intensity than the transferred graphene on SiC for either substrate termination.

Interestingly, graphene lineshapes can readily be observed at 1 ML; albeit the spectrum from graphene ML transferred to the C face substrate is dominated by the substrate itself, with a high presence of the C-Si bonds. However, at 4ML, the expected graphitic spectra is observed in both terminations.

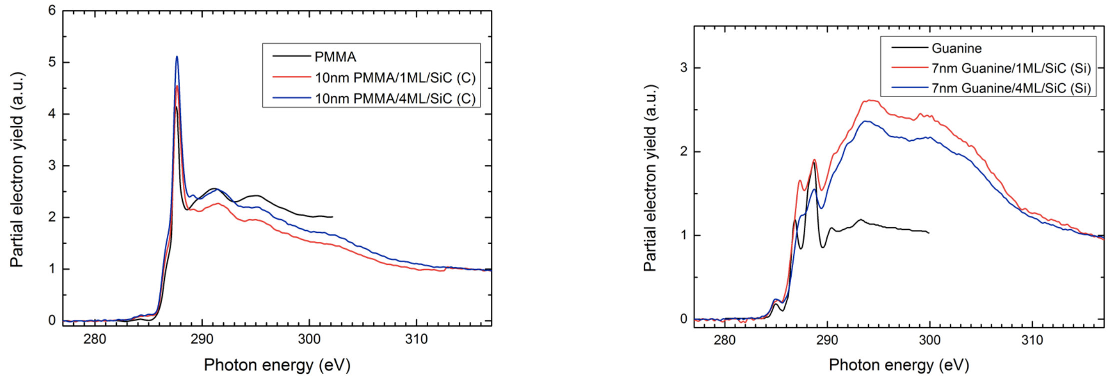


Figure 2 above shows spectral signatures upon 10 nm deposited PMMA and 7 nm deposited guanine on C and Si- terminated substrates respectively. Reference PMMA and guanine data (black) has been extracted from the literature for comparison.
Clearly PMMA dominates all spectra (Figure 2 left) both for 1 and 4 ML graphene; with prominent π* C=O signal ~ 288eV and σ* C-C structure at 291-294 eV. The small intensity just below 290eV is attributed to the broad C-Si signal on SiC. The presence of graphene, either 1 or 4 ML is hardly revealed in these scans; possibly due to a thick dielectric layer with high density. Albeit, the chemical quality of the overlayer is high, and there is no indication of severe disruptions in the structure.

When guanine is deposited on Si-terminated SiC, the presence of graphene is observed in both 1 and 4 ML devices. This is possibly due to a thinner deposited layer, where the signal is less absorbed. Indeed, specific C-H signals can be observed from 1 and 4 ML, at higher energy than the 287 eV emission from pristine guanine. The rich texture between 291 and 310 eV is also attributed to graphene, as can be easily compared with Figure 1 left.
Although a computational approach is needed to fully deconvolute all signals involved in the spectrum, the presence of the distinctive guanine's π* C=O at 288 eV, inclusive of a peculiar shoulder on the low-energy end, suggests that the quality of the desposited guanine is high, without deleterious interactions with the graphitic underlayer.

<u>Conclusions</u>

CVD-grown graphene seems electronically healthy upon transfer to SiC substrates, as evidenced by a visible π* emissions from C=C at 285 eV. The spectroscopic signatures of SiC with C and Si terminations lead to distinctive spectra from 1 ML graphene, but to comparable spectra from 4 ML graphene, with additional C-H groups being observed in the C-terminated face. The question arises as per the processing of the SiC wafers; whether the imaged susbtrates are in fact, representative of the very same surfaces where graphene deposition took place. In applications where 1ML graphene is needed, the Si-terminated surface is recommended, as it resembles more closely to that of native graphene on SiC; albeit, with increased C-H and C=O impurities. In applications where 4 ML of graphene is needed, NEXAFS spectra yields little preference in the choice of substrate termination.

Structural and chemical analysis suggest healthy dielectric epilayers. The presence of graphene is more visible from the thinner epilayer (guanine) and on going theory efforts offer promise to deconvolute the contribution of the different actors to the overall spectrum.

Given the novelty of this approach, perhaps a recommended course of action would involve analysis of both failed and optimized devices; to help identify chemical and structural markers in the overall structure.